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# The study of the ferroelectric phase transition in nanoscale sodium nitrite by the method of thermal noise

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**Abstract**

The ferroelectric phase transition for bulk and nanosized sodium nitrite was studied by the thermal noise method. It was shown that the intrinsic noise generated in the samples at frequencies above 10 MHz near the ferroelectric phase transition follows the behavior of the dielectric constant. The noise level in the loaded MCM-41 films with unidirectional pores was approximately twice as large as that for the pressed samples.



*Keywords*: ferroelectrics; nanostructural materials; thermal noise

## 1. Introduction

Recently, a great deal of attention was focused on the study of nanostructured composites, in particular, nanoporous matrices with different materials embedded into their pores. Physical properties of small particles formed within the matrix are influenced by various size effects associated with sizes and geometry of the pore network. In addition, the pore filling, the interaction between confined particles as well as between particles and matrix walls play a significant role.

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Dielectric studies of nanocomposites with sodium nitrite ferroelectric particles are presented in a number of papers (see [1-3] and references therein). The majority of publications is devoted to the study of sodium nitrite embedded into pores of synthetic opals, porous glasses, and molecular sieves MCM-41 and SBA-15. Films of porous alumina were also used as a porous matrix.

Mezoporous silicate matrices MCM-41 have a hexagonal honeycomb structure with the thickness of walls $h_W = 0.6 – 0.8$ nm and a calibrated size of pore channels. A specific channels surface ~ $10^3$ $m^2$/g, a specific volume of pore lattice is about ~1 $cm^3$/g. According to the electron microscopy data a pore size can change from 2 to 40 nm, depending on the used technology.

In this paper we present the results of studies of nanostructured $NaNO_2$ confined within silicate MCM-41 films with unidirectional pore system. The obtained results are compared with data for bulk sodium nitrite.

## 2. Samples and experiment

In order to get the films, the surfactant cetyltrimethylammonium bromide (STAB) was added into the reaction mixture containing a solid phase precursor, tetraethoxysilane in the dissolved form. Under certain conditions, surfactant molecules self-assemble into stable identical structures (micelles) depending on the nature of the surfactant and the composition of the reaction mixture. The sol-gel reaction involving STAB led to the formation of regular nanostructures. After that the surfactant was removed by heat treatment and a solid mesoporous skeleton remained. The film was formed on the surface of aluminum foil and was 5 – 10 microns thick with a system of unidirectional pores of 3 – 4 nm in diameter. $NaNO_2$ was embedded into the pores from aqueous solution, and then the samples were heated up to the melting temperature of sodium nitrite to remove the residual water. One electrode was an aluminum substrate, the second was vacuum sputtered silver. For comparison, we used $NaNO_2$ pressed samples and MCM-41 (3.7 nm) pressed samples with embedded sodium nitrite in the form of tablets with a diameter of 12 mm and thickness of 1 mm.

Due to strong nonlinearity near the Curie temperature the classical methods of measuring the dielectric constant of ferroelectric materials in thin films are incorrect. For instance, for measurements in applied voltage of 0.1 V on films with thickness of 10 microns, electric fields of about $10^5$ V/cm occur in the film. To avoid this difficulty, some authors suggested receiving the dielectric constant from the noise measurements. In ionic crystals, the thermal motion of ions leads to polarization fluctuations which generate the noise voltage on the electrodes. The spectral density of the voltage fluctuations for linear systems is usually calculated using the Nyquist formula

$$S(\omega) = 4kTRe\{Z(\omega)\} \qquad (1)$$

where Z (ω) is the impedance of the sample. However, the Nyquist formula can not be directly applied to ferroelectrics near the Curie point.

First theoretical studies of noise near the ferroelectric phase transition were presented in [4]. In [4,5] the authors, using the approach based on the Nyquist and Kramers – Kronig formulas, showed that the noise voltage was proportional to the dielectric constant. In this paper, the recording noise method is applied to study the MCM-41 thin films with sodium nitrite and to compare temperature dependences of noise generation with temperature variations of the dielectric constant.

The noise signal was measured by means of a selective low-noise amplifier. A selective voltmeter B6-10 was used as a preliminary unit. The noise level of the device itself without the samples did not exceed ~0.7 μV. The samples under study were put in a thermostat. The studies were carried out in the automated mode; computer and ZetLab software being used. The temperature and voltage noise were measured upon slow heating or cooling the sample every second, so that the interval of one degree corresponded to about one hundred points. The function diagram for the experiments is shown in Fig. 1.

## 3. Results and discussion

Studies show that the intrinsic noise of the samples near the ferroelectric phase transition depends strongly on the frequency and amounts to a few microvolts at frequencies greater than 5 MHz. In this case, the shape of the curve *U(T)* for the pressed samples reproduces the temperature variations of the permittivity at a given frequency. Fig. 2 shows graphs of the noise voltage for the pressed polycrystalline $NaNO_2$.sample, MCM-41pressed sample filled with sodium nitrate and MCM-41 film with $NaNO_2$. One can see from Fig. 2 that the noise level in the MCM-41 films is approximately twice as high as that for the pressed samples. This increases the sensitivity of noise measurements in the film.

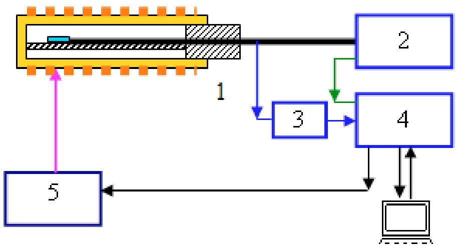


Fig. 1. The function diagram for the experiments: 1– thermostat with a sample, 2 – selective amplifier (B6-10), 3 – direct current amplifier (Z-411), 4 – ADC/DAC (Z-210), 5 – current source with a regulator

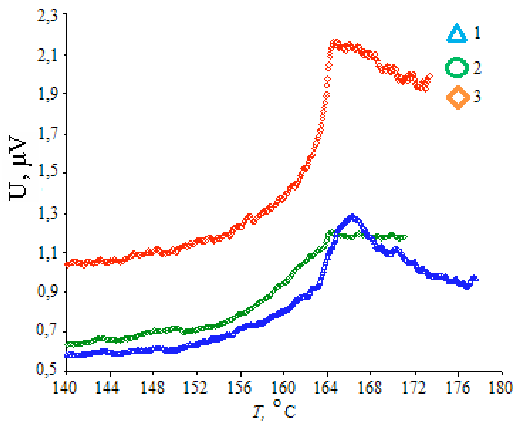


Fig.2. The U(t) for the pressed polycrystalline NaNO2 (1), pressed sample of MCM-41 with sodium nitrate (2) and the film MCM-41 with $NaNO_2$ (3) at 30 MHz ($\Delta f$ = 1 kHz)

The temperatures of maxima of noise generation in the samples under study coincided with temperatures where the maximal values of dielectric susceptibility were observed. Those maxima of noise generation are shifted to low temperatures for sodium nitrite embedded into pores of the MCM-41 film and pressed MCM-41 filled with sodium nitrite compared to that in bulk $NaNO_2$. Such a shift evidences that the ferroelectric phase transition in sodium nitrite confined to pores of MCM-41 film and MCM-41 powder is reduced by about 2 degrees relative to the transition temperature in bulk sodium nitrite.

The sign of the shift agrees with predictions of phenomenological theoretical models based of the Landau expansion [6,7]. These models predict the decrease of the ferroelectric phase transition temperatures which becomes more pronounced with decreasing the pore size. However, the shift of the phase transition for confined sodium nitrite is very small in spite of narrow pores-channels in MCM-41 mesoporous sieves.

One should emphasize that the phase transition shift is negative for sodium nitrite embedded into unidirectional pores in the MCM-41 film while for sodium nitrite introduced into unidirectional pores of porous alumina the shift of the ferroelectric phase transition was positive [2]. The difference between the behavior of sodium nitrite in MCM-41 thin films and within porous alumina can arise due to much bigger interpore distance in porous alumina which allowed considering particles within it as independent while we cannot neglect the interparticle coupling in close channels of the MCM-41 sieves. However, this question requires more studies to be clarified.

## 4. Conclusions

The studies of noise generation in comparison with dielectric susceptibility for two kinds of nanoconfined sodium nitrite and bulk $NaNO_2$ showed that the temperature dependences of noise generation reproduce those of dielectric susceptibility. This can be considered as an experimental confirmation of theoretical approach presented in Ref. [4,5] and opens new opportunities for investigations of dielectric properties of nanostructured composites, in particular, of composite thin films. The temperature of the ferroelectric phase transition for sodium nitrite embedded into a MCM-41 film decreased relative to the transition point for bulk sodium nitrite by the same amount as for sodium nitrite in the pressed MCM-41 powder. This result contrasts with data for sodium nitrite in the porous alumina, in which the increase of temperature transition was observed. Clarification of what causes different signs of the transition shift for sodium nitrite within the MCM-41 and porous alumina films despite the unidirectional nature of pores in both cases needs in additional studies while one could suggests that the interparticle coupling plays an important role.

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